Control of Interfacial and Electrical Properties of Metal/Pr-oxide/Ge Gate Stack Structures

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1. Introduction

For high performance Ge MOSFETs, we focus on Pr-oxide as a higher-k gate dielectric, since Pr-oxide has a high dielectric constant more than 30 and it can realize a low leakage current density (J_g) [1-4]. In the metal/Pr-oxide/Ge gate stack structures, the interface structures and bulk structures in the Pr-oxide film have crucial impacts on dielectric constant, interface state density (D_{it}) , and J_g , since Pr-oxide has some crystalline structures relating to the Pr valence state such as Pr^{3+} and Pr^{4+} . Therefore, we focus on the control of the chemical bonding structure among Pr, Ge, and O. In this study, we demonstrated the control of interfacial and crystalline properties of Pr-oxide/Ge stacked structures with the incorporation of nitrogen (N). We also investigated the effect of unique character of gate metals for oxidation-reduction reaction on the Pr-oxide/Ge interface structures.

2. Results and discussion

We have demonstrated the effect of N incorporation to the Pr-oxide/Ge interface by formation of a Ge₃N₄ interlayer with radical nitridation technique [5] to control the O concentration and interfacial structures. A Pr-oxide film was formed on the Ge₃N₄ layer with ALD method using Pr(EtCp)₃ precursor and isopropyl-alcohol (IPA) [6]. The XPS depth analysis reveals the N segregation at the Pr-oxide/Ge interface and the Ge diffusion to the surface of the Pr-oxide film [6,7] (Fig. 1). This result means that the Pr-oxynitride is formed by the N incorporation at the Pr-oxide/Ge interface, resulting in decreasing the O concentration at the interface. Also, incorporation of N at the interface causes the change in the Pr valence state from Pr⁴⁺ to Pr³⁺. In other words, we can control the interface structures by incorporating N. These structural changes drastically improve the electrical interface properties (Fig. 2). As a result, N incorporation can give a low D_{it} value of 3×10^{11} eV⁻¹cm⁻².

We investigated the interfacial reactions during the formation of metal films and annealing of the metal/Pr-oxide/Ge structures by using hard X-ray photoelectron spectroscopy. The formation and decomposition reactions of Ge oxide strongly depend on the oxidation-reduction characters of metal film. In particular, the normalized intensity of Ge oxide to Ge substrate peak for the Al/Pr-oxide/Ge sample is smaller than that of the sample without a metal film (Fig. 3). This suggests that some amount of Ge oxide is reduced by the strong reduction character of Al.

3. Conclusions

Incorporation of N to the Pr-oxide/Ge interface is effective to control the O concentration and the Pr valence state in the Pr-oxide film. Consequently, the N incorporation can realize the good electrical properties. Selection of gate metal species with basing on oxidation-reduction character is quite important to control the Pr-oxide/Ge interfacial reactions since the Ge oxide is reduced by the strong reduction character of the gate metal.

References

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Fig. 1 Depth profiles of the composition ratio for the Pr-oxide/Ge sample with a nitride interlayer measured by XPS with Ar ion surface sputtering.



Fig. 2 *C-V* characteristics of the Al/Pr-oxide/Ge MOS capacitors (a) without and (b) with a nitride interlayer measured at 190 K with a high frequency of 1 MHz.



Fig. 3 Peak area intensity ratio of Ge oxide to Ge substrate in $\text{Ge2p}_{3/2}$ photoelectron core spectra of the metal/Pr-oxide/Ge gate stack structure measured by hard X-ray photoelectron spectroscopy (hv=7939 eV).